

# Adsorptions studies with CO<sub>2</sub> at 195 K - theory and practice

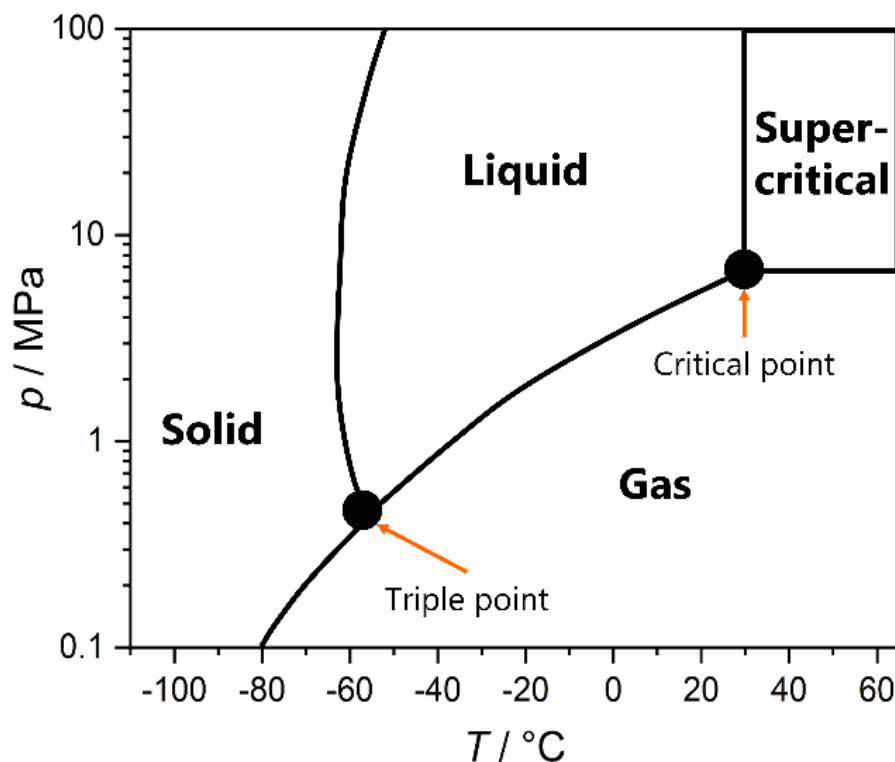
## Introduction

Sorption studies with CO<sub>2</sub> are still in the spot light of current research projects. Not only because of climate related investigations but also to characterize nano-sized and porous materials. Close to real-life conditions of CO<sub>2</sub> adsorption of gas mixtures are typically gained with dynamic method methods, such as breakthrough curves. However, single component isotherms are mostly collected via static manometric methods. Despite the fact that is common practice, one might varying characteristic data. One reason might be the fact that CO<sub>2</sub> does not form a liquid phase under norm conditions.

Within this study we aim to show

- an easy way to conduct CO<sub>2</sub> measurements
- the nature of the adsorbed phase using the mesoporous model material MCM-41
- substance parameters for CO<sub>2</sub>

In a common evaluation of N<sub>2</sub> or Argon isotherms, it is obvious to assume a liquid phase of both gases in the adsorbate phase. Therefore, the Gurvitch rule can be applied to calculate the pore volume by using the liquid density of the adsorbate. A glimpse on the phase diagram of CO<sub>2</sub> (Figure 1) reveals however, that a liquid phase of CO<sub>2</sub> exists only at high pressures. Under ambient pressure CO<sub>2</sub> directly transforms from the solid phase to the gas phase, it sublimates. Basically, the liquid density could not be used to calculated material parameters. But is there really no liquid phase inside the pores of the material?



**Figure 1.** Phase diagram of carbon dioxide: The liquid phase exists only at elevated pressure, namely 0.52 MPa at minus 56.56 °C (triple point); below the triple point, there is no liquid phase even at elevated pressure

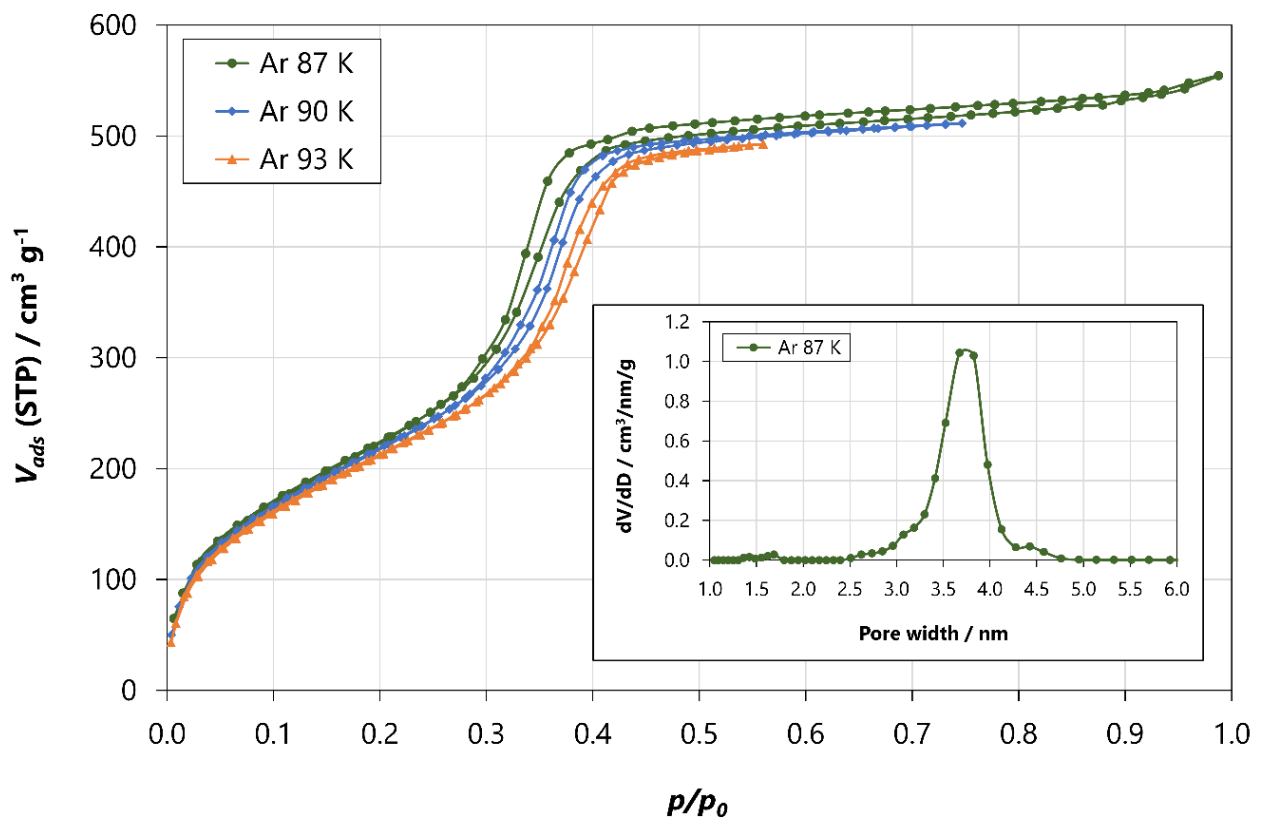
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As mentioned above CO<sub>2</sub> is subject of numerous adsorption studies. However, there is no consensus in the literature as to which vapor pressure of CO<sub>2</sub> should be used. Some authors assume the sublimation pressure of solid CO<sub>2</sub> for measurements below the triple point of 216.59 K (-56.56 °C).<sup>[1, 2]</sup> Others used the vapor pressure of the undercooled liquid<sup>[3, 4]</sup> to represent the data and to calculate parameters such as specific surface area or pore size distribution.

Within our LabSPA (Lab of Scientific Particle Analysis) department of 3P Instruments we therefore studied the adsorption behavior of MCM-41 with CO<sub>2</sub> and for comparability and argumentative reasons also with Argon Argon. In detail, CO<sub>2</sub> isotherms are recorded in a broad temperature range from 180 K up to 205 K. The measurement possibilities for the determination of CO<sub>2</sub> isotherms result on the one hand from the vapor pressure of dry ice and on the other hand from the maximum pressure of an available analyzer. Argon isotherms are collected at 87 K, 90 K and 93 K. All isotherms were measured on a 3P micro 300. The temperature was controlled with a cryoTune 87 (Ar measurements) and a cryoTune 195 (CO<sub>2</sub> measurements) respectively. Both show a temperature constancy smaller than 0.004 K.

Figure 2 shows the Argon isotherms at 87 K, 90 K and 93 K. The pore size distribution can be calculated from the isotherm at 87 K using the NLDFT approach, resulting in a mean value of 3.8 nm and a maximum of 4.8 nm, which is in good agreement with the literature.<sup>[5]</sup>

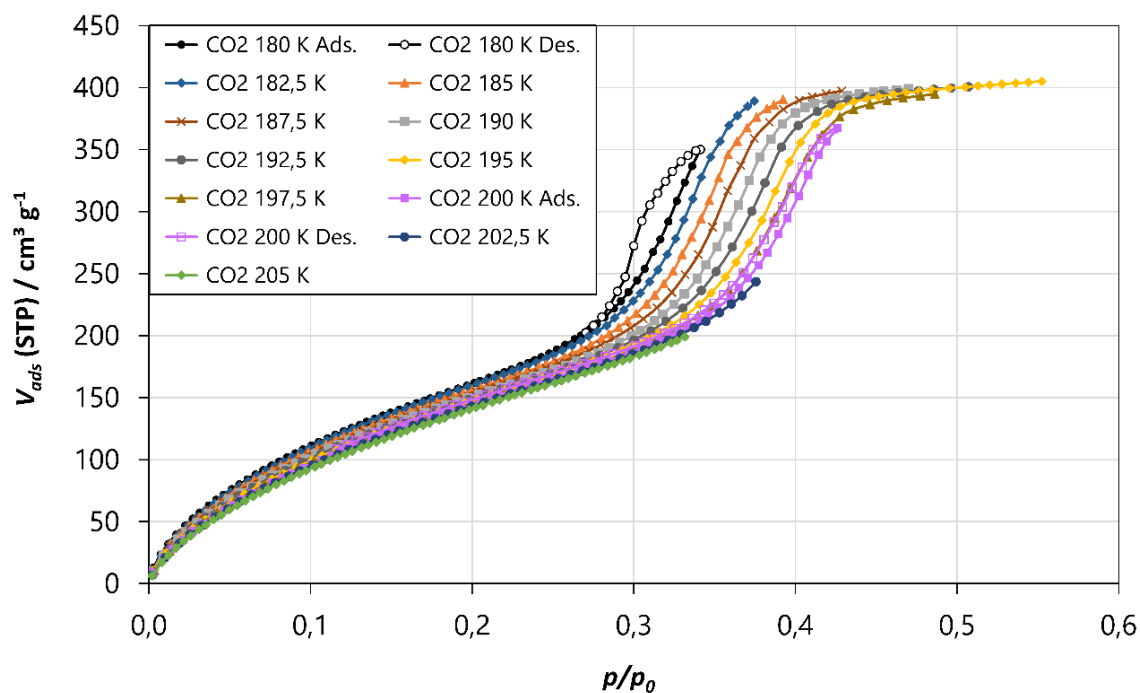


**Figure 2.** Argon isotherm at 87 K, 90 K and 93 K, inset shows the pore size distribution calculated from the isotherm at 87 K using an NLDFT approach

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In Figure 3 the set of CO<sub>2</sub> isotherms in the temperature range from 180 K up to 205 K are shown. A first look reveals that both temperature extrema result only in a partial pore filling. Below 185 K it is due to the formation of dry ice (resublimation of CO<sub>2</sub>) in the sample cell. Above 200 K in contrast the resulting vapor pressure of CO<sub>2</sub> is the limiting factor. As a result, the isotherms in the range from 185 K up to 200 K can be used to characterize the surface area and to determine the isosteric heat of adsorption.



**Figure 3.** CO<sub>2</sub> isotherms from 185 K up to 205 K in 2.5 K steps, for clearness only the adsorption branch is shown, all isotherms show comparable hysteresis loops as shown exemplarily for the isotherms at 180 K and 200 K

A complete filling of the 4.8 nm pores can be achieved for MCM-41 at 195 K (Figure 3), whereas it is shown in the literature<sup>[6]</sup> that no mesopores > 5 nm are filled by CO<sub>2</sub> at 195 K for a CMK-3 material. From this, it can be concluded that the threshold value is around 5 nm, i.e. larger pores are not detected by CO<sub>2</sub> at 195 K, whereas smaller pores can be characterized very well.

Moreover, the pores of MCM-41 are filled in the same pressure range ( $p/p_0 = 0.3 - 0.4$ ) with both Ar and CO<sub>2</sub> (Figure 2 and Figure 3). If the  $p_0$  of dry ice (solid CO<sub>2</sub>) would be applied to plot the isotherms, the relative pressure range of the pore filling would be shifted to  $p/p_0 = 0.15 - 0.22$ . Thus, it can be shown that the application of the saturation pressure of the undercooled liquid of CO<sub>2</sub> is more reasonable for the evaluation of CO<sub>2</sub> isotherms.

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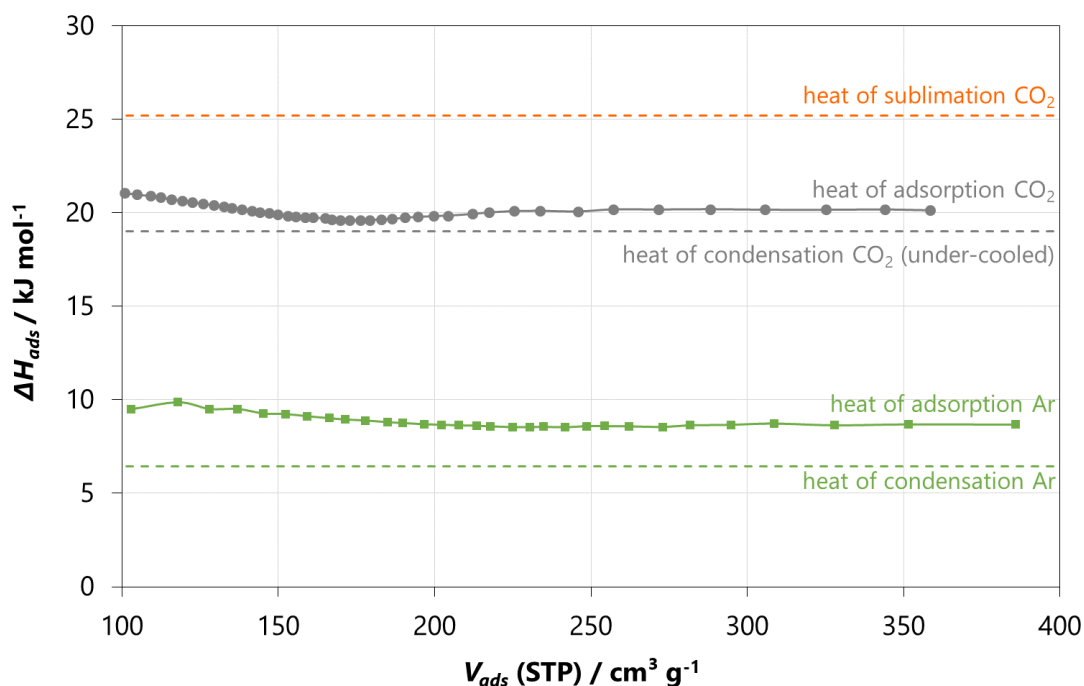
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**Table 1.** Calculated Pore volume of MCM-41 dependent on the adsorbate properties

Isotherm	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]	used adsorbate density from
Ar 87 K	0.64	liquid argon
CO <sub>2</sub> 195 K	0.63	undercooled CO <sub>2</sub> liquid
CO <sub>2</sub> 195 K	0.51	solid CO <sub>2</sub> (dry ice)

This is also shown by the calculation of the pore volume (Table 1). If the density of the undercooled liquid of CO<sub>2</sub> is used for this calculation, almost identical values result for Ar and CO<sub>2</sub>. However, if the density of solid CO<sub>2</sub> is used, this value deviates considerably (20%).

From the set of isotherms shown in Figure 2 and Figure 3 the isosteric heat of adsorption can be calculated by using the Clausius Clapeyron equation (Figure 4). For both gases the heat of adsorption is above the heat of condensation, which account to 19 kJ mol<sup>-1</sup> for undercooled CO<sub>2</sub> and 6.4 kJ mol<sup>-1</sup> for Argon respectively. Furthermore, the heat of adsorption of CO<sub>2</sub> on MCM-41 over the complete isothermal range is clearly smaller than the heat of sublimation of solid CO<sub>2</sub> (25.2 kJ mol<sup>-1</sup>) and thus once again indicates a liquid-like adsorbate phase.



**Figure 4.** Isosteric heat of adsorption of MCM-41 in the range of the pore filling, calculated from the CO<sub>2</sub> and Ar isotherms, plotted lines show the heat of condensation and sublimation for comparison

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Following points can be concluded from this study:

1. a measurement of CO<sub>2</sub> at 195 K allows the characterization of pores smaller than 5 nm, even with a normal pressure sorption device
2. below the triple point of CO<sub>2</sub>, the adsorbate has a liquid-like state, at least in pores smaller than 5 nm
3. a direct comparison with Ar isotherms proves the reasonable application of the vapor pressure and density of undercooled CO<sub>2</sub> for the description of CO<sub>2</sub> isotherms
4. the wide temperature range for both CO<sub>2</sub> and Ar could be adjusted very easily and especially very precisely with the cryoTune technology. The cryoTune series can be used not only with sorption instruments from 3P Instruments but also with sorption analyzers from other instrument manufacturers.
5. Recommended substance data for CO<sub>2</sub> at 195 K are summarized as
  - a. non-ideality coefficient: 0.000202 kPa<sup>-1</sup>
  - b. Saturation pressure of undercooled liquid<sup>[7]</sup>: 188 kPa
  - c. Density of adsorbate phase: 1.258 g cm<sup>-3</sup>
  - d. Cross-sectional area of CO<sub>2</sub> adsorbate molecule<sup>[8]</sup>: 0.170 nm<sup>2</sup>

## References

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